(3+3)-Annulation of Carbonyl Ylides with Donor-Acceptor Cyclopropanes: Synergistic Dirhodium(II) and Lewis Acid Catalysis

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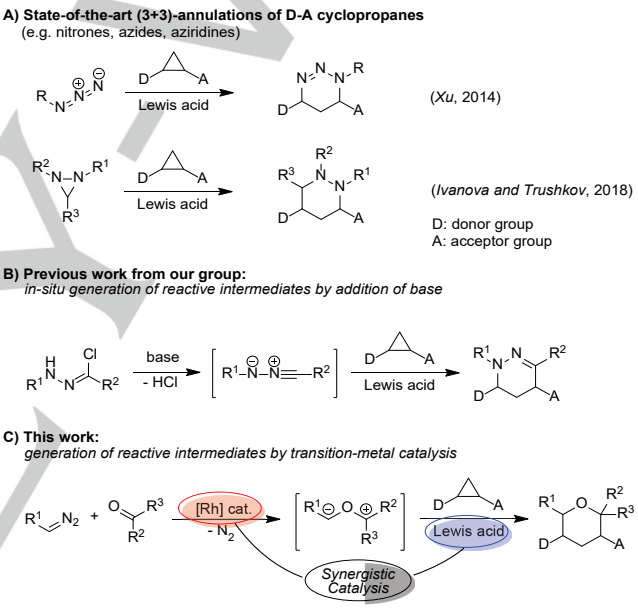
Abstract: *The first (3+3)-annulation process of donor-acceptor cyclopropanes using synergistic catalysis is reported. The $Rh_2(OAc)_4$-catalyzed decomposition of diazo carbonyl compounds generated carbonyl ylides in situ. These 1,3-dipoles were converted with donor-acceptor cyclopropanes, activated by Lewis acid catalysis, to afford multiply substituted pyran scaffolds in high yield and diastereoselectivity. Extensive optimization studies enabled access to 9-oxabicyclo[3.3.1]nonan-2-one and 10-oxabicyclo[4.3.1]decen-2-ol cores, exploiting solvent effects on intermediate reactivity.*

The efficient one-step synthesis of complex oligocyclic scaffolds from simple building blocks has fascinated organic chemists for decades. Cycloadditions and rearrangements – often combined in a domino fashion – are prime examples of access to molecular complexity in a single synthetic step.[1] Besides alkenes and alkynes, which are the most prominent systems to undergo cycloaddition reactions, donor-acceptor (D-A) cyclopropanes have in numerous cases been successfully involved in such transformations. Their use as 1,3-zwitterionic synthons is promoted by their high strain energy and by the polarized bond between the carbon atoms bearing the donor and the acceptor moiety. After seminal work in this field by Wenkert and Reissig some 30 to 40 years ago, the field has vastly expanded, especially during the last decade, leading to novel protocols of rearrangements, cycloadditions and ring-opening reactions.[2,3] One focus has been the development of (3+n) cycloaddition reactions affording five-, six- and seven-membered rings (n = 2, 3, 4). Most of the (1,n)-dipoles that have been inserted are stable compounds (e.g. aldehydes,[4] imines,[5] allenes,[6] thiocarbonyls,[7] azides,[8] nitrones,[9] diaziridines[10]) or can be generated by the stoichiometric addition of base from a stable precursor (e.g. nitrile imines).[11] To the best of our knowledge, the reaction of D-A cyclopropanes with 1,3-dipoles generated by transition metal catalysis as fleeting intermediates has not been reported yet.[12]

Our idea was to use the dirhodium(II)-catalyzed decomposition of diazo carbonyl compounds to generate carbonyl ylides in situ,[13,14] which are then employed in a (3+3)-cycloaddition reaction with D-A cyclopropanes. Because the three-membered rings are relatively inert, we expected that a second catalyst, a Lewis acid, would be required to activate this second component. Only the use of two distinct catalysts, independently activating the two starting materials (i.e. a synergistic catalytic approach), should allow the desired transformation in a highly efficient manner.[15]



Scheme 1. Literature-known (3+3)-annulation reactions of D-A cyclopropanes and our work using synergistic transition metal and Lewis acid catalysis.

At the beginning of our studies, we chose D-A cyclopropane **1a** and diazo compound **2a** as model substrates to determine the optimal conditions for this synergistic (3+3) cycloaddition. As expected, two catalysts are required for a successful transformation (Table 1, entries 1-2). However, even the use of both a Rh(II) and a Lewis acid catalyst only induces the reaction in the presence of molecular sieves (entries 3-5). The Lewis acid $Sc(OTf)_3$ proved to be more suitable than $Yb(OTf)_3$. Surprisingly, $Sc(OTf)_3$ doped with 5% of $Yb(OTf)_3$ gave about a threefold increase in yield to 32% and a much higher diastereoselectivity of up to 9:1 (entries 4, and 6).[16] However, better yields were only achievable by changing the solvent. Whereas in THF no reaction was observed (entry 7), toluene boosted the yield to 93%, but with only moderate diastereoselectivity (entries 8-10). The optimal reaction temperature was found to be 30 °C; higher temperatures (70 °C) shut down the desired transformation (entry 11). More elaborate dirhodium(II) catalysts such as $Rh_2(pfb)_4$ and $Rh_2(cap)_4$

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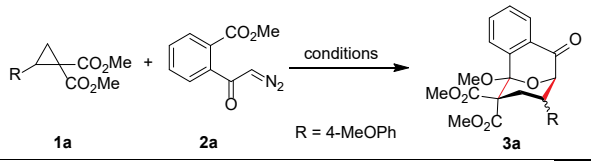
only resulted in worse yields (entries 12-13, for full details on the optimization studies, see Supporting Information).

Table 1. Optimization of the reaction conditions.[a]



1a **2a** **3a**

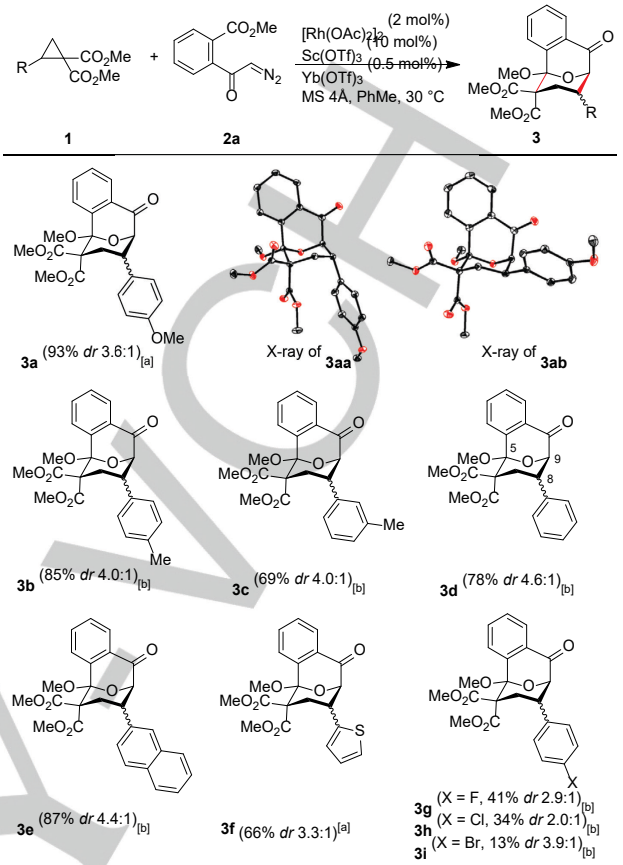
Entry	Rh(II) cat.	Lewis acid	Solvent	T [°C]	**3a** [%]	*dr*
1	$Rh_2(OAc)_4$	-	CH_2Cl_2	RT	0	-
2	-	$Sc(OTf)_3$	CH_2Cl_2	RT	0	-
3[b]	$Rh_2(OAc)_4$	$Sc(OTf)_3$	CH_2Cl_2	RT	0	
4	$Rh_2(OAc)_4$	$Sc(OTf)_3$	CH_2Cl_2	RT	12	4.4:1
5	$Rh_2(OAc)_4$	$Yb(OTf)_3$	CH_2Cl_2	RT	5	7.1:1
6[c]	$Rh_2(OAc)_4$	$Sc(OTf)_3$	CH_2Cl_2	RT	32	9.1:1
7[c]	$Rh_2(OAc)_4$	$Sc(OTf)_3$	THF	RT	0	-
8[c]	$Rh_2(OAc)_4$	$Sc(OTf)_3$	PhMe	RT	83	4.0:1
9[c,d]	$Rh_2(OAc)_4$	$Sc(OTf)_3$	PhMe	0	52	5.0:1
10[c]	**$Rh_2(OAc)_4$**	**$Sc(OTf)_3$**	**PhMe**	**30**	**93**	**3.6:1**
11[c]	$Rh_2(OAc)_4$	$Sc(OTf)_3$	PhMe	70	0	-
12[c]	$Rh_2(pfb)_4$	$Sc(OTf)_3$	PhMe	30	61	3.4:1
13[c]	$Rh_2(cap)_4$	$Sc(OTf)_3$	PhMe	30	62	4.0:1

[a] Reaction conditions: **1a** (150 µmol), $Sc(OTf)_3$ (10 mol%), MS 4Å (60 mg), **1a** was dissolved in 2 mL of solvent and a solution of **2a** (100 µmol) in 1 mL of solvent was added within 1 h. [b] No MS 4Å was added. [c] $Sc(OTf)_3$ was doped with $Yb(OTf)_3$ (0.5 mol%). [d] 20 mol% $Sc(OTf)_3$ and 1 mol% $Yb(OTf)_3$ were used. Isolated yields. THF = tetrahydrofuran, pfb = perfluorobutyrate, cap = ε-caprolactamate.

With the optimized reaction conditions in hand, we investigated the scope of this (3+3) cycloaddition reaction. First, a variety of D-A cyclopropanes were investigated (Scheme 2). Phenyl donors with electron-donating substituents (**1a**, **1b**, **1c**) yielded the desired products **3a-3c** in good to excellent yields. More extended π-systems such as naphthyl (**1e**) and heterocyclic donors such as thienyl (**1f**) were also tolerated, whereas more electron-withdrawing fluoro, chloro and bromo substituents decreased the performance of the reaction significantly (**3g-i**). Attempts to involve D-A cyclopropanes with strongly electron-withdrawing 4-nitro- or 4-cyanoaryl moieties and non-aromatic donors such as vinyl residues in this protocol were unsuccessful.

In addition, the carbonyl ylide substrates were varied (Figure 1). Extended π-systems (**3j**), heterocycles (**3l**, **3m**) and electron-withdrawing substituents attached to the aromatic backbone (**3k**) work in moderate to good yields. Substrates lacking an aromatic backbone were not successfully converted into the respective oxygen-bridged carbocycles **3**.

To obtain an insight into the mechanism, the reaction of **1b** with **2a** was performed with enantioenriched D-A cyclopropane (96% *ee*). The resulting annulation product **3db** shows 94% *ee* and its absolute configuration (5*R*,8*R*,9*R*) was elucidated by X-ray diffraction analysis.[17] This result suggests a stereospecific annulation process (Scheme 3; for further details see Supporting Information).



Scheme 2. Scope of the (3+3)-annulation for various D-A cyclopropanes **1**. [a] **1** (150 µmol) and **2** (100 µmol) were used. [b] **1** (100 µmol) and **2** (150 µmol) were used. The annotation **a** represents the axial and **b** the equatorial isomer.

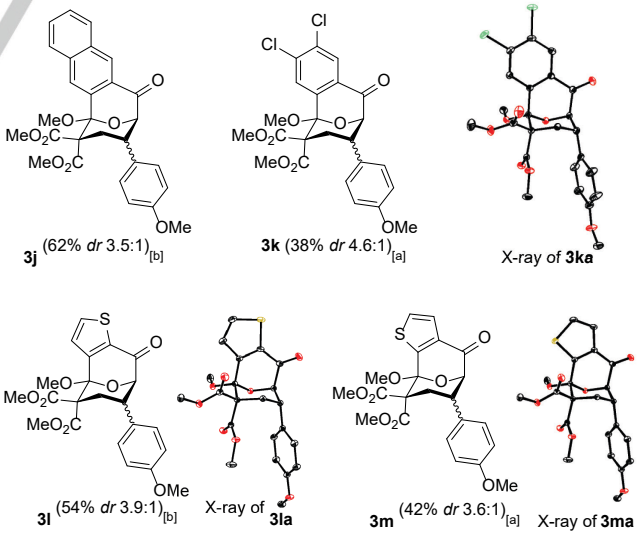


Figure 1. Scope of the (3+3)-annulation with respect to different carbonyl ylides. [a] **1** (150 µmol) and **2** (100 µmol) were used. [b] **1** (100 µmol) and **2** (150 µmol) were used. The annotation **a** represents the axial and **b** the equatorial isomer.

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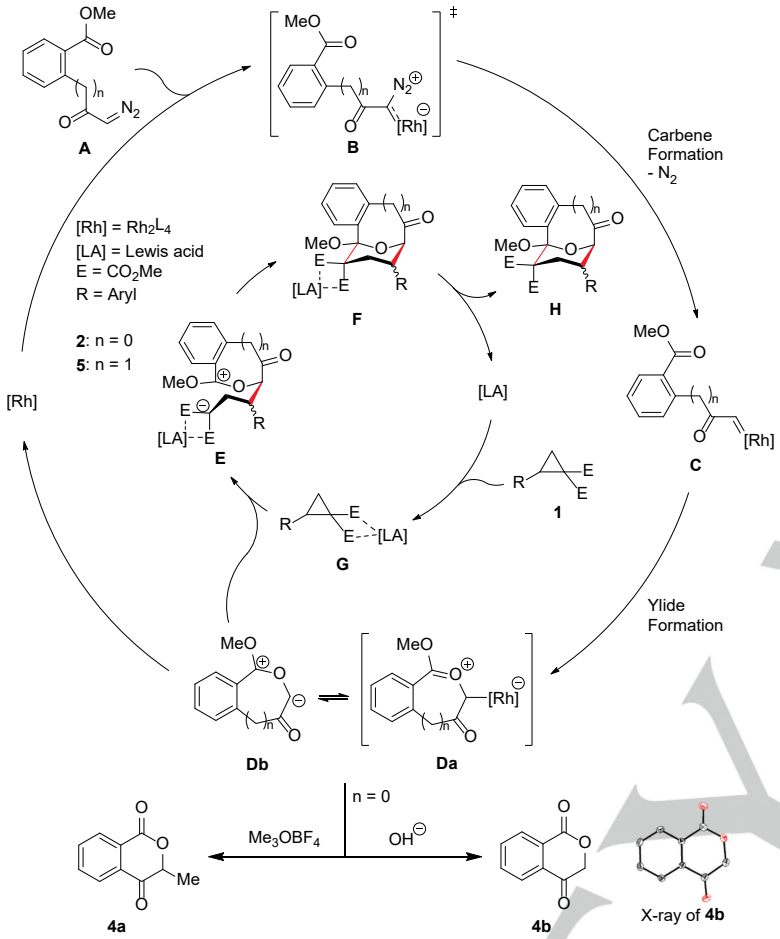


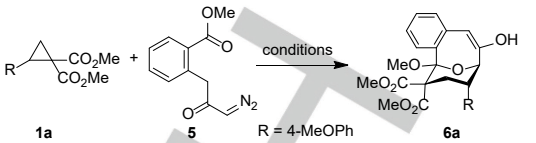
Scheme 3. Plausible mechanism for the synergistic (3+3)-annulation reaction of D-A cyclopropanes **1** with in situ generated carbonyl ylides **C**.

Additional trapping experiments of the active species generated from **2a** were performed in the absence of both cyclopropane **1** and Lewis acid. They delivered alkylated and non-alkylated isochromanones **4a** and **4b**, respectively. From these results we infer that species **D** merge the outer carbenoid cycle with the inner D-A cyclopropane cycle as depicted in Scheme 3. Once formed from metallacarbenoid species **C**, they react with activated D-A cyclopropane **G** to afford **E**, followed by ring-closure to **F**.[16] The inner cycle completes after release of product **H**.

Minor changes to the initial procedure (Table 2) together with a homolog of the diazo starting material allowed access to nine-membered oxygen-bridged products. Surprisingly, the reaction of D-A cyclopropanes **1** with diazo compound **5** furnishes the products **6** as cyclononenoles (Scheme 4), in contrast to the expected cyclononanones, though in high yield and excellent diastereoselectivity.

In contrast to the reaction with diazo compounds **2**, it turned out to be more tolerant towards electron-withdrawing substituents and heteroatom donors. Notably, halogen-substituted donors (**6d-6f**) as well as heterocyclic or nitrogen donors as commonly used by Waser (**6g** and **6i**) were tolerated.[4b,5c,7d]

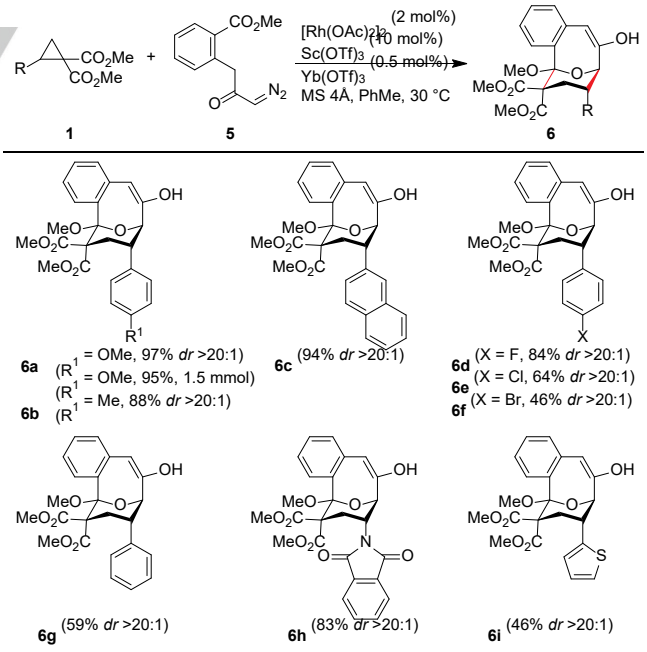
Table 2. Readjustment of the reaction conditions.[a]



Entry	Solvent	T [°C]	**6a** [%]	*dr*
1	PhMe	30	37	>20:1
2	PhMe	50	37	>20:1
3[b]	PhMe/THF (1:1)	30	0	-
4[c]	CH_2Cl_2	30	70	>20:1
5[d]	**CH_2Cl_2**	**30**	**97**	**>20:1**

[a] Reaction conditions: To MS 4Å (60 mg), $Rh_2(OAc)_4$ (2 mol%), $Sc(OTf)_3$ (20 mol%) and $Yb(OTf)_3$ (1 mol%) a solution of **1a** (150 µmol) in 2 mL of solvent was added. A solution of **5** (100 µmol) in 1 mL of solvent was added within 5 h. [b] **1a** (100 µmol) and **5** (150 µmol) were used. [c] **1a** (200 µmol) were used. [d] No work-up was performed. Yields represent isolated yields. THF = tetrahydrofuran.

The strikingly different diastereoselectivities for both transformations are probably associated with solvent effects, which strongly influence reactivity and appearance of intermediate species (**Da** or **Db**) that are catalytically active. It is known that CH_2Cl_2, rather than toluene, stabilizes the formation of metallacarbenoid species.[18] Thus, we assume that the bulky paddlewheeled dirhodium in **Da** forces the donor substituent of the former cyclopropane to the most remote, i.e. axial, orientation. The fact that high diastereoselectivities for **6a** are also observed in toluene can be attributed to the more puckered structure of the seven-membered 1,3-dipole **Db** (n = 1) in contrast to its six-membered counterpart (n = 0).



Scheme 4. Scope of oxygen-bridged cyclononenoles **6** via (3+3)-annulation. **1** (200 µmol) and **5** (100 µmol) were used.

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In summary, we have developed a protocol for the reaction of D-A cyclopropanes and carbonyl ylides. To realize this transformation, we have made use of synergistic dirhodium and Lewis acid catalysis; the former catalyst generated carbonyl ylides in situ from corresponding diazo compounds, while $Sc(OTf)_3$ activated the three-membered ring. 9-Oxabicyclo[3.3.1]nonan-2-one and 10-oxabicyclo[4.3.1]decene-2-ol cores have been obtained in moderate to excellent yields and diastereoselectivity. A strong solvent influence with respect to the stereochemical outcome was observed, suggesting different reactive species as key intermediates. Trapping experiments and investigations with highly enantioenriched D-A cyclopropane led us to a plausible mechanistic concept.

Acknowledgments

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cyclopropanes • cycloaddition • carbonyl ylides • donor-acceptor systems • synergistic catalysis

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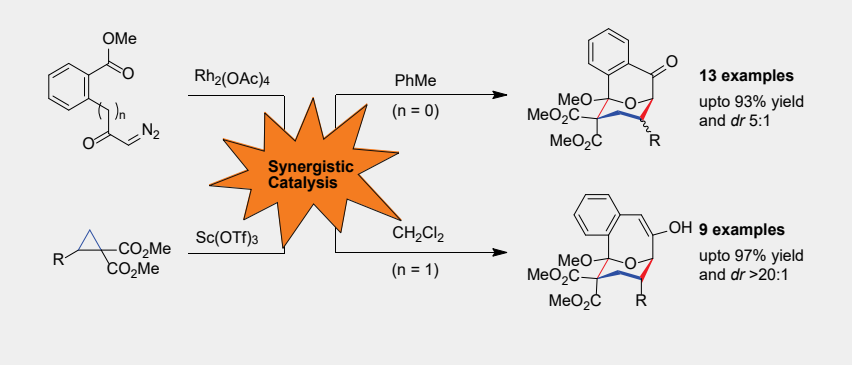
[16] We anticipate that $Yb(OTf)_3$ increases the electrophilicity of the benzylic position in intermediate **E**, thus directing the reaction to the desired intermediate **F**, since no formation of open-chain products was observed.

[17] Details of X-ray structure determinations are given in the Supporting Information. Additionally, CCDC 184659-184665 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[18] a) J. Wang, J. Kubicki, H. Peng, M. S. Platz, *J. Am. Chem. Soc.* **2008**, *130*, 6604; b) D. M. Hodgson, J. M. Bailey, C. Villalonga-Barber, M. G. B. Drew, T. Harrison, *J. Chem. Soc., Perkin Trans. 1* **2000**, 3432.

COMMUNICATION



Best of both worlds: A synergistic catalytic approach for the construction of multiply substituted pyrans is reported. It merges cyclopropane with carbene chemistry. The synthesis of [3.3.1]- and [4.3.1]-core structures under mild conditions in moderate to excellent yields is demonstrated and a plausible mechanism is suggested.

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(3+3)-Annulation of Carbonyl Ylides with Donor-Acceptor Cyclopropanes: Synergistic Dirhodium(II) and Lewis Acid Catalysis

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